G = three dimensional spectral energy distribution function for the scalar fluctuations, Equation (4)
k = wave number, cm.$^{-1}$
N_r = rotational speed of impeller
N_o = zero count for turbulent fluctuations, that is the number of times a second that the turbulent fluctuation crosses zero
n_f = frequency, cycles/sec.
Q = absolute value of mass velocity
t = time
u_i, u_j, u_k = i, j, k, components of velocity fluctuation
u_o = root mean square of velocity fluctuation Equation (1)
V_{avg} = time average mean voltage signal
ΔV = root mean square voltage fluctuation
ΔV_f = fraction of total root mean square voltage fluctuation per unit frequency step, that occurs at the chosen frequency n_f
v_l = volume of tap water fed into vessel per unit time
v_r = volume of fluid recirculated by impeller per unit time
v_t = volume of tracer fed into vessel per unit time
λ_c = Eulerian micro time scale for concentration fluctuations
λ_T = Eulerian micro time scale for velocity fluctuations
Φ = concentration fluctuation energy spectral distribution function based on frequency, Equation (6)

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Gaseous Counterdiffusion in Catalyst Pellets

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To assist in evaluating the role of internal pore diffusion in limiting the overall reaction rate in heterogeneous catalysis the rate of diffusion without reaction may be measured on the catalyst particle of interest, and an effective diffusion coefficient may be calculated. The convenient assumption is that the same effective diffusion coefficient applies to the differential equations for diffusion with chemical reaction under the same conditions of temperature, pressure, and chemical species. This approach was suggested by Damköhler (*5*) and expanded by Wheeler (*27*) and Wagner (*25*). An alternate approach of Thiele (*23*) has been less frequently used in recent research.

The effective diffusion coefficient depends on the properties of the gases, on the temperature and pressure, and on the pore structure of the catalyst. Since the measurements are made without chemical reaction, the measurement conditions must differ from the reaction conditions. The effective diffusion coefficient must be extrapolated over wide ranges of temperature and pressure and to different chemical species. To this end one often employs a tortuosity factor, which is the reciprocal of the ratio of the measured effective diffusion coefficient to the diffusion coefficient which applies to the fluid within the pores at the same conditions. It is then assumed that the tortuosity factor depends only on the catalyst pore structure.

Whether or not the tortuosity approximation is used, it cannot be disputed that an understanding of the diffusion mechanism within the pores is essential to the proper interpretation of diffusion data. This paper is intended to clarify that mechanism for the important case of binary gaseous diffusion.

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Of particular concern here is the experimental technique which is usually credited to Wicke and Kallenbach (*29*). The ends of a catalyst particle, usually a cylindrical pellet, are exposed to two gas streams flowing at steady state. The faces of the pellet are generally maintained at equal total pressures, and one or both of the gas streams leaving the pellet are analyzed. From the analysis and the measured flow rate of the stream the flux of gas through the pellet can be calculated. The method may be called *steady counterdiffusion.* Early measurements of this type were made by Buckingham (*3*) on porous soils; more recent measurements on adsorbents, catalysts, and other synthetic porous media include those of Wicke and Kallenbach (*29*), Weisz (*26*), Dubik (*7*), Roiter and Korneichuk (*17*), Hoogschagen (*13*), Scott and Cox (*20*), Henry and co-workers (*12*), Scott and Dullien (*22*), and Evans and co-workers (*8*).

MECHANISMS OF GASEOUS DIFFUSION

Two limiting conditions are recognized for gaseous diffusion: Knudsen diffusion, in which the molecules collide much more frequently with the pore walls than with each other; and bulk diffusion, which ensues when the mean free path between intermolecular collisions is small compared with the pore diameter. At constant temperature and pressure, a Knudsen diffusion coefficient may be defined by

$$\vec{N}_A = -c\, D_{KA} \nabla X_A \qquad (1)$$

It can be shown (*4*) that

$$D_{KA} = \frac{4}{3} K_{0A} \bar{u}_A \qquad (2)$$

where K_{0A} is a Knudsen permeability or flow constant which depends primarily on the properties of the porous medium; it is approximately proportional to a characteristic pore diameter. In accordance with Equations (1) and (2) the Knudsen diffusion coefficient is independent of the total pressure, and the flux of a component is inversely proportional to the square root of its molecular weight.

The description of bulk diffusion requires careful attention to the use of the proper flux in defining the diffusion coefficient. From molecular theory (*2*) the bulk binary gaseous diffusion coefficient is defined by

$$\vec{J}_A^* = -c\, \mathcal{D}_{AB} \nabla X_A \qquad (3)$$

Similarly

$$\vec{J}_B^* = -c\, \mathcal{D}_{BA} \nabla X_B = -\vec{J}_A^* \qquad (4)$$

It follows that

$$\mathcal{D}_{AB} = \mathcal{D}_{BA} \qquad (5)$$

Note that the flux $\vec{J}_A^*$ is a local flux with respect to the molar average velocity, while the measured flux $\vec{N}_A$ is taken with respect to fixed coordinates. Although the law of conservation of mass requires that $\vec{N}_A$ be uniform at steady state, no such restriction applies to $\vec{J}_A^*$. The relation between the fluxes is given by

$$\vec{N}_A = \vec{J}_A^* + C_A \vec{V}^* = \vec{J}_A^* + X_A\,(\vec{N}_A + \vec{N}_B) \qquad (6)$$

Equation (6) with $\vec{N}_B$ equal to zero will be recognized as the starting point for problems of diffusion through a stagnant film.

In describing measurements of steady counterdiffusion many investigators have assumed equimolal counterdiffusion:

$$\vec{N}_B = -\vec{N}_A \qquad (7)$$

With this assumption Equations (3) and (6) reduce to Fick's first law:

$$\vec{N}_A = -c\, \mathcal{D}_{AB} \nabla X_A \qquad (8)$$

However equimolal fluxes in steady counterdiffusion have never been observed experimentally. Trautz and Müller (*24*) and Hoogschagen (*13*) contend that the ratio of the fluxes is beyond the experimenter's control; the flux ratio adjusts itself to satisfy the law of conservation of momentum. Hoogschagen's theory predicts that the fluxes are inversely proportional to the square roots of the molecular weights in bulk diffusion as well as in Knudsen diffusion, and also in the intermediate range between the two limits.

Only Hoogschagen (*13*), Henry and co-workers (*12*), Evans and co-workers (*8*), and Scott and Cox (*21*) report measurements of both fluxes in steady counterdiffusion. All of these investigations observed the fluxes to be approximately inversely proportional to the square roots of the molecular weights. Hoogschagen showed that his data fell outside of the Knudsen range, and Scott and Cox and Evans and co-workers proved that their data were in the bulk range. The diffusion range cannot be verified for the data of Henry and co-workers; their assertion that their data lie in the Knudsen range is based on the assumption that bulk diffusion would be equimolal, an assumption which is not tenable in view of the other experimental observations cited above. The present work sought to clarify this issue by measuring both fluxes over a range of total pressures sufficiently broad to cover the intermediate range.

The transition from Knudsen to bulk diffusion encompasses a thousandfold range of mean free paths; the lack of attention to the intermediate range belies its importance. Typical process conditions fall in the intermediate range when the pore diameter is about 1μ, a size common to the macropores in pelleted catalysts. Two theories of self diffusion in the intermediate range have been suggested: Bosanquet's additive resistance law (*14*)

$$\frac{1}{D_A} = \frac{1}{D_{KA}} + \frac{1}{\mathcal{D}_{AA}} \qquad (9)$$

and Wheeler's exponential combining rule (*27*)

$$D_A = \mathcal{D}_{AA}\,[1 - \exp(-D_{KA}/\mathcal{D}_{AA})] \qquad (10)$$

Neither expression has been tested experimentally. The Bosanquet formula states that the resistance to transport is the sum of the resistance due to wall collisions and to intermolecular collisions; Equation (9) agrees very closely with a more rigorous expression derived from molecular theory by Pollard and Present (*14*).

In general the gas-phase diffusion is augmented by surface transport of adsorbed molecules. Surface transport is neglected in the following theoretical development; it shall be seen that the surface flux is unimportant in the experiments reported here.

THEORY

A theory of binary diffusion in the intermediate range for diffusion through a porous medium with negligible surface transport and with equal total pressures at opposite ends of the particle will now be developed. The corresponding theory for a cylindrical tube is given elsewhere (*18*).

An effective diffusion coefficient for all ranges is defined by

$$\vec{J}_A^* = -c\, D_{AB} \nabla X_A \qquad (11)$$

The author defines a diffusion tortuosity for bulk diffusion by

$$(\vec{J}_A^*)_{\text{bulk diffn.}} = -\frac{\epsilon \mathcal{D}_{AB}}{q_D}\, c \nabla X_A \qquad (12)$$

The tortuosity q_D differs from that used by other investigators in that it is defined specifically with respect to bulk diffusion. A new Knudsen diffusion coefficient is defined by

$$(\vec{J}_A^*)_{\text{Knudsen diffn.}} = -\mathcal{D}^K{}_{AB}\, c \nabla X_A \qquad (13)$$

With this definition

$$\mathcal{D}^K{}_{AB} = \mathcal{D}^K{}_{BA} = D_{KA}\,[1 - X_A\,(1 - R_{AB})] \qquad (14)$$

where R_{AB} is the flux ratio N_B/N_A. In contrast to the coefficient D_{KA} the new coefficient $\mathcal{D}^K_{AB}$ depends on mole fraction. Although the former coefficient may be used for problems entirely in the Knudsen range, the new coefficient is more convenient for the intermediate range.

To develop a combining law which expresses D_{AB} in terms of $\mathcal{D}_{AB}$ and $\mathcal{D}^K_{AB}$ the Stefan-Maxwell momentum balance method (*15*) is used. A momentum balance on the molecules of species A is made in a differential volume element by equating the net flux of momentum carried in and out of the volume element to the loss of momentum by transfer to the walls and by transfer to molecular of species B. For bulk diffusion this method leads to the well-known Stefan-Maxwell equations. The theoretical development is given in the appendix;
the result is

$$\frac{1}{D_{AB}} = \frac{q_D}{\epsilon \mathcal{D}_{AB}} + \frac{1}{\mathcal{D}^K_{AB}} \tag{15}$$

Equation (15) is analogous to the additive resistance law for self diffusion, Equation (9). An equivalent form is obtained by substitution of Equation (14) into (15) and the rearrangement:

$$D_{AB} = \frac{(\epsilon \mathcal{D}_{AB}/q_D)\,[1 - X_A\,(1 - R_{AB})]}{N_{KnA} + [1 - X_A\,(1 - R_{AB})]} \tag{16}$$

In steady counterdiffusion the flux N_A is measured. From Equations (6) and (11) this flux is

$$\vec{N}_A = - \frac{D_{AB}\, c\, \nabla X_A}{[1 - X_A\,(1 - R_{AB})]} \tag{17}$$

By substitution of (16) into (17) one obtains for the z component

$$N_A = \frac{-(\epsilon \mathcal{D}_{AB}/q_D) c}{N_{KnA} + 1 - X_A\,(1 - R_{AB})}\,\frac{dX_A}{dz} \tag{18}$$

By integration of Equation (18)

$$\left(\frac{N_A L}{c}\right)\left(\frac{q_D}{\epsilon \mathcal{D}_{AB}}\right)(1 - R_{AB}) = \ln\left[\frac{N_{KnA} + 1 - X_{AL}\,(1 - R_{AB})}{N_{KnA} + 1 - X_{A0}\,(1 - R_{AB})}\right] \tag{19}$$

For the special case in which N_{KnA} is zero and q_D/ϵ is 1, Equation (19) is identical to an equation derived by Trautz (*24*) for bulk diffusion.

Two other independent derivations of Equation (19) have been published. Scott and Dullien (*22*) derived the equivalent equation for empty tubes by momentum-balance arguments similar to those employed here. Evans, Watson, and Mason (*9*) used a model which considers the porous medium to consist of giant dust molecules which are uniformly distributed and fixed in space. Although their definition of the effective diffusion coefficient differs slightly from that used here, Equation (18) can be recovered exactly by combining their Equations (13), (14), and (30). The integrated expression presented here, Equation (19), is identical to their Equation (37).

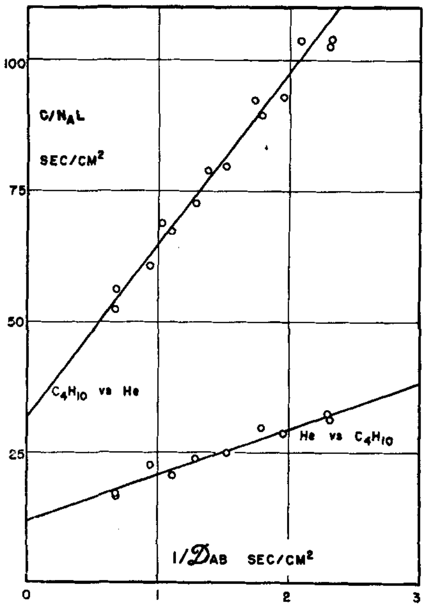

Fig. 1. Steady counterdiffusion of isobutane and helium.

Frequently measurements are made with pure gases contacting opposite ends of the pellet. Then X_{AL} is zero and X_{A0} is 1, and

$$\left(\frac{N_A L}{c}\right)\left(\frac{q_D}{\epsilon \mathcal{D}_{AB}}\right)(1 - R_{AB}) = \ln\left[\frac{N_{KnA} + 1}{N_{KnA} + R_{AB}}\right] \tag{20}$$

An approximate expression which agrees with Equation (20) to within a few per cent is

$$\frac{cD_{KA}}{N_A L} = 1 + \frac{1}{N_{KnA}}\left(\frac{R_{AB} - 1}{\ln R_{AB}}\right) \tag{21}$$

Equation (21) was developed intuitively. The first term gives the flux for the limit of Knudsen diffusion, while the second term is the limiting form of (20) for bulk diffusion. If R_{AB} is independent of pressure, then Equation (21) predicts that $cD_{KA}/N_A L$ varies linearly with pressure. If all of the data are in the Knudsen range, the slope is zero; if the data fall in the bulk range, the second term is much greater than 1 and the intercept is essentially zero.

Since the effective diffusion coefficient depends on mole fraction, D_{AB} does not appear explicitly in any of the integrated expressions, Equations (19) to (21). Unless the experiment is run with gases of nearly equal concentration contacting opposite ends of the particle, D_{AB} varies with z, and no single value of D_{AB} may be calculated from a measurement of the fluxes. However the constants q_D and K_{0A} may be calculated by applying Equation (21) to data at several total pressures. For this purpose Equation (2) may be used to write Equation (21) and a similar equation for $cD_{KB}/N_B L$ in the form

$$\frac{c}{N_A L\sqrt{M_A}} = \frac{\kappa c}{N_B L \sqrt{M_B}} = \frac{3}{4K_{0A}\sqrt{8RT/\pi}} + \frac{q_D}{\epsilon \mathcal{D}_{AB}\sqrt{M_A}}\left(\frac{R_{AB} - 1}{\ln R_{AB}}\right) \tag{22}$$

where

$$\kappa = \frac{K_{0B}}{K_{0A}} = R_{AB}\sqrt{\frac{M_B}{M_A}} \tag{23}$$

Thus a graph of $c/N_A L\sqrt{M_A}$ and $\kappa\, c/N_B L\sqrt{M_B}$ vs. $(R_{AB} - 1)/\mathcal{D}_{AB}\sqrt{M_A}$ ln R_{AB} should be linear. The parameter κ represents the deviation of the flux ratio from Hoogschagen's principle that the fluxes are inversely proportional to the square roots of the molecular weights. It is assumed that κ is independent of pressure.

It must be emphasized that the effective diffusion coefficient defined by Equation (11) is a differential diffusion coefficient, in contrast to the integral effective diffusion coefficient proposed by other investigators. Thus Scott and Dullien (*22*) suggest calculation of a mean diffusion coefficient by elimination of N_A between Equation (19) and the integrated form of Fick's first law:

$$N_A = \frac{c\, D_n}{L}\,(X_{A0} - X_{AL})$$

An integral diffusion coefficient so calculated will apply to steady counterdiffusion but not in general to diffusion with chemical reaction. This follows from the dependence of the differential diffusion coefficient on con-

TABLE 1. MEASURED FLUX RATIOS FOR A SERIES OF RUNS WITH ISOBUTANE-HELIUM

Run no.	Pressure in. Hg	Flux ratio N_B/N_A
179	7.90	3.06
176	10.90	2.70
177	14.94	3.02
180	20.94	3.04
178	26.77	3.11
Mean		2.99
Std. devn.		0.16

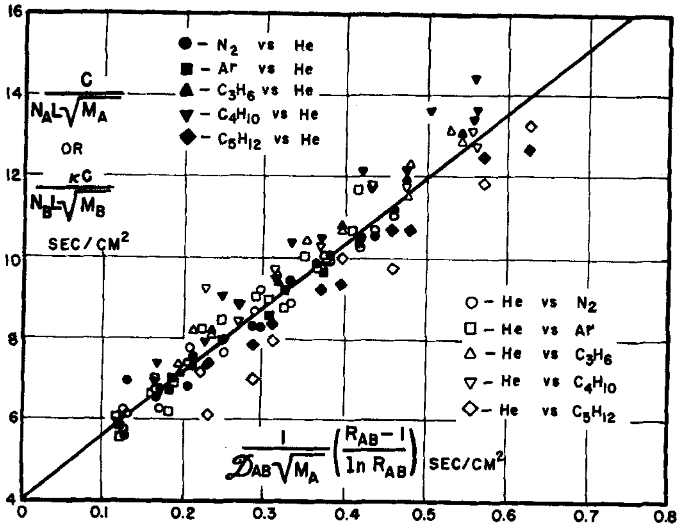

Fig. 2. Diffusion data for five binary systems.

centration; the concentration distribution which accompanies a chemical reaction differs from that in steady counterdiffusion without reaction. In calculating the effectiveness factor the theoretical development must begin with a differential equation based on Equations (11) and (16). Since the present theories of the effectiveness factor assume that the diffusion coefficient is independent of mole fraction, these theories apply only to the Knudsen range.

EXPERIMENTAL EQUIPMENT AND MATERIALS

The equipment was similar to that of Weisz (*26*), except that both gas streams were analyzed. Runs were made at room temperature with five different binary gas systems, each of five test gases (nitrogen, argon, propylene, isobutane, and neopentane) diffusing against helium. In the symbols used below the subscript *A* refers to the test gas, *B* to helium. Each system was studied at five total pressures between 200 and 700 mm. Hg, and both thermal conductivity analyzers were calibrated at each pressure.

The range of Knudsen numbers was

$$0.76 < N_{KnA} < 4.9$$
$$0.24 < N_{KnB} < 1.3$$

Since the Knudsen number is proportional to T/P, the same ranges would apply to data at 1 atm. and temperatures from 25° to 770°C. for the same systems on the same catalyst. Although the data here were taken at room temperature and reduced pressure, these conditions simulate those of process interest.

The porous particles were ⅛ in. by ⅛ in. (nominal) cylindrical pellets of an alumina catalyst support. Actual dimensions of the particle used for most of the measurements were length, 0.3447 cm.; diameter, 0.3264 cm.; mass, 44.4 mg. The reported length is the maximum length; no correction was made for the slightly convex nature of the ends of the pellet. The pore-size distribution was measured by mercury penetration (*6, 16*) and carbon tetrachloride adsorption (*1*). The pellets have a bidisperse pore system similar to that of the pellets studied by Henry and co-workers (*12*). The macropore volume distribution has a peak at a diameter of 1.25 μ, the micropore at 120 Å. The total pore volume, 0.357 cc./g., is 52% of the pellet volume, and about 65% of the pore volume is in the micropores. Of the total B-E-T surface area of 76 sq. m./g. about 99% is estimated to be in the micropores.

Adsorption isotherms for the three hydrocarbons are available (*18*). The maximum relative pressures are 0.6 for neopentane, 0.3 for isobutane, and 0.08 for propylene. The adsorption data for isobutane and neopentane are well correlated by the B-E-T equation. Measurements with neopentane were held to pressures below the capillary condensation region.

EXPERIMENTAL RESULTS

The original data are tabulated elsewhere (*18*).

Table 1 shows the flux ratios observed for a typical set of runs. The fluxes are unequal, and the flux ratio is approximately independent of pressure; this result was observed for all five systems. Table 2 compares the observed flux ratios with the theoretical ratios $\sqrt{M_A/M_B}$. Only in the system nitrogen-helium is the flux ratio close to the theoretical.

Figure 1 is a graph of c/N_AL and c/N_BL vs. $1/\mathcal{D}_{AB}$ for the system isobutane-helium; the abscissa is proportional to the total pressure. This graph is typical of those observed for all systems. The data fall on separate, nonparallel lines for each gas. Since neither the slopes nor the intercepts are zero, the data are in the intermediate range. The linearity of the graphs confirms the absence of surface transport, for the surface flux would not be expected to vary in a simple way with pressure. Notice that the graphs are not parallel, as they would be if equimolal counterdiffusion were approached at high pressures.

In Figure 2 the data for all five systems are plotted in the form of Equation (22), $c/N_AL\sqrt{M_A}$ and $\kappa c/N_BL\sqrt{M_B}$ vs. $(R_{AB} - 1)/\mathcal{D}_{AB}\sqrt{M_A} \ln R_{AB}$. Similar graphs were obtained for nitrogen-helium on two other pellets. The constants κ and R_{AB} are taken from Table 2. Virtually all of the data for all five gas pairs fall within 10% of the single least-square line. From the slope and intercept of this line K_{OA} is 7.41 × 10^{-7} cm. with standard deviation 3.2%, and q_D/ϵ is 15.9 with standard deviation 2.3%. The standard deviation of the data points from the line is 0.53, which is 5.8% of the mean ordinate. With these constants Equation (15) may be written for this pellet:

$$\frac{1}{D_{AB}} = \frac{15.9}{\mathcal{D}_{AB}} + \frac{1}{9.88 \times 10^{-7}\,\bar{u}_A\,[1 - X_A\,(1 - R_{AB})]} \qquad (24)$$

DISCUSSION

To verify Equation (15) for the effective diffusion coefficient it would be desirable to perform steady counterdiffusion experiments with small differences in mole fraction. With the data at hand only the integrated expression, Equation (22), can be tested. The latter equation is well confirmed by the data.

For the usual case in which pure gases counterdiffuse it is not possible to calculate a single value of the effective diffusion coefficient from steady counterdiffusion data. To calculate the constants q_D/ϵ and K_{OA} both fluxes must be measured over a range of

TABLE 2. COMPARISON OF OBSERVED AND THEORETICAL FLUX RATIOS

(Mean flux ratios are based on several series of runs for each system.)

System, *A-B*	Mean observed flux ratio, R_{AB}, (N_B/N_A)	Theoretical flux ratio, $(\sqrt{M_A/M_B})$	κ, $(R_{AB}\sqrt{M_B/M_A})$
N_2-He	2.86	2.65	1.079
Ar-He	3.75	3.16	1.187
C_3H_6-He	3.01	3.24	0.929
C_4H_{10}-He	3.08	3.78	0.815
C_5H_{12}-He	3.11	4.25	0.732

pressures. If the fluxes are measured at only one pressure, the information obtained is insufficient. Measurement of one flux at several pressures is also inadequate, since one does not yet know how to estimate R_{AB}. Equimolal counterdiffusion does not occur, and most of the systems studied here deviate considerably from Hoogschagen's theoretical estimate.

The failure of the flux ratio to equal $\sqrt{M_A/M_B}$ seems to be unique to this study. Since the departure is greatest with the hydrocarbons (though also significant with argon), it is tempting to attribute the deviations to surface transport of adsorbed vapors. But this explanation agrees neither with the observation that the flux ratio is independent of pressure nor with the linearity of the graphs of Figure 1. On the basis of published studies of surface transport [for example (*11*)], the surface flux would be expected to vary strongly with pressure. With the high adsorptions encountered here (relative pressures up to 0.6) this variation should be strongly nonlinear. Now since the surface flux is not necessarily additive to the gas flux, one cannot prove that surface transport is definitely absent. However the observation that the flux ratio is independent of pressure makes this assumption seem very safe.

Curiously the deviations from Hoogschagen's theoretical flux ratio seem to appear in the flux of helium rather than the flux of test gas. Thus K_{oA} is the same for all five test gases diffusing against helium, but K_{oB} (that is $\kappa\ K_{oA}$) varies for helium diffusing against different gases. This unusual phenomenon calls for further research.

From the nonzero slopes and intercepts of Figure 1, it is known that the data obtained here lie in the intermediate range. Data on the flow of pure gases through the same pellets (*18*) also fall in the intermediate range, and the mean pore diameter estimated from the flow data is nearly the same as the peak macropore diameter obtained from the pore-size distribution. These results suggest that the measured diffusion occurs almost entirely in the macropores, with their mean pore diameter of about 1μ; Knudsen diffusion would be the expected mechanism in the micropores. The controlling role of the macropores can be explained by the plausible hypothesis that in a straight-through diffusion or flow experiment the resistances of the macropores and micropores combine in parallel.

The absence of surface transport becomes more understandable in terms of a parallel combination of macropores and micropores. By calculations (*18*) based on the Gilliland-Baddour-Russell (*11*) theory of surface transport it can be shown that in macropores about 1 μ in diameter the surface flux should be negligible compared with the gas flux; in micropores about 100 Å in diameter the surface flux is of the same order of magnitude as the gas flux, but the sum of the two micropore fluxes is still much less than the macropore flux.

The investigation of diffusion reported here is part of a broader study of diffusion and flow in catalyst pellets (*18*). Inferences concerning the pore structure of the pellet, based on the relation between the diffusion and flow measurements, will be published elsewhere. The more important implications follow.

1. The flow of pure gases can be related to steady counterdiffusion; K_{oA} and q_D/ϵ can be estimated from flow measurements.

2. In bidisperse pore systems diffusion and flow occur mainly in the macropores if these are much larger than the micropores. The macropores then serve as distribution channels, while the micropores provide almost all of the surface area and the reaction sites.

3. The high tortuosities reported in the literature may be due to incorrect evaluations of the diffusion mechanism. The resistance to diffusion in the intermediate range is the sum of two resistances; the calculated tortuosity will be too high if it is incorrectly assumed that only one of the resistances is controlling.

4. High tortuosities will also be calculated for bidisperse pore systems if the calculation is based on the total porosity rather than the macroporosity when the diffusion occurs through the macropores only. For the catalyst studied here q_D is 8.3 based on the total porosity of 0.52; based on the macroporosity of 0.18, q_D is 2.9, which is much closer to the tortuosity calculated from flow data, 2.4. After reevaluation of the mechanisms for published diffusion data in terms of the theory presented here the author estimates tortuosities between 1.2 and 1.6 for other catalysts.

5. When chemical reaction occurs within a catalyst pellet, the flux ratio is determined by the stoichiometry of the reaction. Most theories of the effectiveness factor are based on a flux written as in Equations (1) and (8), that is Fick's first law. This formulation is strictly valid only for Knudsen diffusion, for dilute gases ($X_A = 0$), or for binary reactions with no change in the number of moles, such as isomerization ($N_B = -N_A$). The theories must be modified if they are to be applied more generally in the bulk and intermediate ranges.

6. Since the flux ratio determined by the stoichiometry may differ from the flux ratio required to satisfy the law of conservation of momentum at uniform pressure, internal pressure gradients may accompany chemical reactions, as suggested by Hoogschagen (*13*). Approximate calculations show these gradients to be significant whenever the Thiele modulus is greater than 1 if the pore diameter is less than 1 μ. Recent progress on the subject of diffusion with a pressure gradient has been reported by Wicke and Hugo (*28*) and by Evans and co-workers (*10*).

CONCLUSIONS

The flux ratio in steady counterdiffusion is independent of pressure and different from unity; the ratio cannot be used as a criterion to distinguish Knudsen diffusion from bulk diffusion. Since the flux ratio deviates from Hoogschagen's theoretical estimate, additional research is required to elucidate the factors which determine the ratio. A theoretical expression for the effective diffusion coefficient in the intermediate range, Equation (15), has been derived; the coefficient depends on mole fraction. Equation (22) for the fluxes, which is based on this effective diffusion coefficient, has been verified experimentally. The constants K_{oA} and q_D/ϵ in Equation (15) may be evaluated from steady counterdiffusion experiments in which both fluxes are measured over a range of pressures.

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NOTATION

c = total molar concentration (moles/L^3)

$\mathfrak{D}_{AB}$ = binary bulk diffusion coefficient for system A-B (L^2/t)

$\mathfrak{D}^K_{AB}$ = Knudsen diffusion coefficient, Equation (13) (L^2/t)

D_A = effective diffusion coefficient for self diffusion in intermediate range (L^2/t)

D_{AB} = effective diffusion coefficient for binary diffusion in a porous medium (L^2/t)

D_{KA} = Knudsen diffusion coefficient, Equation (2) (L^2/t)

$\vec{J}_A^*$ = molar flux of species A relative to molar average velocity, based on total cross-sectional area (moles/tL^2)

K_{0A} = Knudsen flow permeability constant (L)

L = length of sample (L)

M_A = molecular weight of species A (M/mole)

M_{ij} = momentum lost by species i per unit time per unit volume by collisions with species j (M/L^2t^2)

M^o_{ij} = M_{ij} at $N_{Kni} = 0$ (bulk diffusion) (M/L^2t^2)

M_{iw} = momentum lost by species i per unit time per unit volume by collisions with pore walls (M/L^2T^2)

M^∞_{iw} = M_{iw} at $N_{Kni} = \infty$ (Knudsen limit) (M/L^2t^2)

$\vec{N}_A$ = molar flux of species A with respect to stationary coordinates, based on total cross-sectional area (moles/$t\ L^2$)

N_{KnA} = Knudsen number for diffusion $= \dfrac{3\epsilon \mathcal{D}_{AB}}{4q_D K_{0A} \overline{u_A}}$

P_i = partial pressure

q_D = diffusion tortuosity

R = gas law constant $(ML^2/t^2T$ mole)

R_{AB} = flux ratio, N_B/N_A

T = absolute temperature (T)

$\overline{u}_A$ = equilibrium mean molecular speed of species A, $\sqrt{8RT/\pi M_A}$ (L/t)

$\vec{V}^*$ = molar average velocity = $X_A\vec{V}_A + X_B\vec{V}_B$

$\vec{V}_A$ = drift velocity of species A (L/t)

X_A = mole fraction of species A

X_{AL} = X_A at $z = L$

X_{A0} = X_A at $z = 0$

z = axial distance coordinate (L)

ϵ = porosity

κ = $K_{0B}/K_{0A} = R_{AB}\sqrt{M_B/M_A}$

π = 3.14159 - - - -

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APPENDIX

Derivation of Equation (15)

Consider a one-dimensional, isothermal porous medium at steady state and uniform total pressure, containing a multicomponent gas mixture. The following is assumed: (*a*) shear stresses are negligible; (*b*) the gases obey the ideal gas law and Dalton's law of partial pressures; (*c*) the concentrations and drift velocities are functions of the axial coordinate only, and there are no transverse drift velocities; (*d*) the squares of the drift velocities are much less than the mean square thermal velocities. Two additional assumptions will be introduced below. Also it may be shown (*18*) that under these assumptions the existence of equal total pressures at opposite ends of the sample is adequate to ensure uniform total pressure.

Now perform a balance of z-momentum on the molecules of species i in a differential slice of the porous medium parallel to the faces and perpendicular to the z axis. The slice has unit total cross-sectional area and thickness dz. It is shown elsewhere (*18*) that under assumption (*d*), the flux of z momentum carried by species i across a fixed plane normal to the z axis is P_i. The net flux of z momentum carried in and out of the slice by molecules of species i is the sum of the z momentum transferred to the walls and the z momentum transferred to molecules of other species:

$$-\epsilon\frac{dPi}{dz} = M_{iw}\,dz + \sum_j M_{ij}\,dz \quad (A1)$$

It is now assumed that (*e*) $M_{iw} = M^\infty_{iw}$ for all N_{Kni}, and (*f*) $M_{ij} = M^o_{ij}$ for all N_{Kni}. Then

$$-\epsilon\frac{dPi}{dz} = M^\infty_{iw} + \sum_j M^o_{ij} \quad (A2)$$

The momentum transferred to the walls at infinite Knudsen number is known from the theory of Knudsen flow (*4*):

$$M^\infty_{iw} = \frac{3\epsilon N_i RT}{4K_{0i}\overline{u_i}} \quad (A3)$$

From the theory of multicomponent bulk diffusion, suitably modified for porous media

$$M^o_{ij} = \frac{q_D\,P\,X_iX_j}{\mathcal{D}_{ij}}(V_i - V_j) \quad (A4)$$

By substitution of (*A3*) and (*A4*) into (*A2*) and use of the ideal gas law and the uniformity of total pressure

$$-c\frac{dx_i}{dz} = \frac{N_i}{\frac{4}{3}K_{0i}u_i} + \frac{q_D}{\epsilon}\sum_j \frac{(X_jN_i - X_iN_j)}{\mathcal{D}_{ij}} \quad (A5)$$

For a binary system Equation (*A5*) becomes

$$-c\frac{dx_A}{dz} = \frac{N_A}{\frac{4}{3}K_{0A}\overline{u}_A} + \frac{X_BN_A - X_AN_B}{\epsilon\mathcal{D}_{AB}\,q_D} \quad (A6)$$

By use of Equations (2), (6), (11), and (14)

$$\frac{1}{D_{AB}} = \frac{q_D}{\epsilon\mathcal{D}_{AB}} + \frac{1}{\mathcal{D}^K_{AB}} \quad (15)$$

Equation (15) may also be obtained by applying (ϵ) and (*f*) to an expression developed by Rubin (*19*) from the Boltzmann equation. These crucial assumptions are indeed strong; however M_{iw} deviates most widely from M^∞_{iw} when N_{Kni} is small, and then, $M_{iw} << \Sigma M_{ij}$. Similarly M_{ij} departs most widely from M^o_{ij} at large N_{Kni}, where the intermolecular transport terms are small.